

One Step Synthesis of 2-Substituted Benzofuran Derivatives
with Dichlorobis(benzonitrile)palladium

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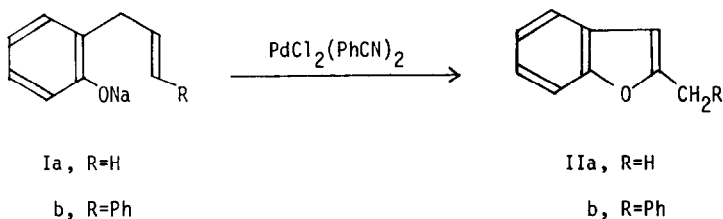
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(Received in Japan 11 January 1973, received in UK for publication 23 January 1973)

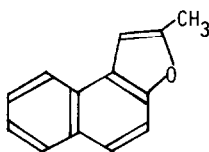
2-Substituted dihydrobenzofurans can be easily formed by the treatment of 2-allylphenols with acid catalysts¹. To our knowledge, however, there is no direct cyclization of 2-allylphenols into 2-substituted benzofurans. We have found that the benzofurans can be prepared cleanly by the reaction of sodium salt of allylphenols and dichlorobis(benzonitrile)-palladium.

Thus, into the suspended solution of sodium salt prepared from 2-allylphenol (Ia, 5 mmol) and sodium methoxide (5 mmol) in benzene (50 ml) was added dichlorobis(benzonitrile)palladium (5 mmol) at room temperature. After 3 hrs refluxing the solution, the resulted palladium black was filtered off and filtrate was concentrated. Distillation gave colorless oil (b.p. 80-82°/20 mm) which was indicated to be only two compounds of 2-methylbenzofuran (IIa) and benzonitrile by VPC analysis. 2-Methylbenzofuran could be easily separated by preparative VPC and identified by the comparison with authentic sample², IIa, n.m.r. (CCl₄) δ 2.36 (d, J=1 Hz, 3H), 6.02 (m, 1H), 7.07 (m, 4H), ν 1610, 1590 cm⁻¹, m/e 132. The yield was 31%³.

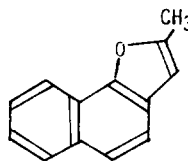


2-Benzylbenzofuran (IIb) could be also obtained by the same treatment of 2-cinnamylphenol and dichlorobis(benzonitrile)palladium as above and could be readily separated by distillation of crude mixture. The yield of IIb was 53 %, IIb, b p 94-95°/4 mm, n m r (CCl₄) δ 3.91 (broad s, 2H), 6.10 (m, 1H), 7.08 (m, 4H), τ r 1600, 1584 cm⁻¹, m/e 208

Similarly, 2-methyl[2,1-b]naphthofuran (III) and 2-methyl[1,2-b]naphthofuran (IV) were also isolated, respectively, from the reactions of 1-allyl-2-naphthol and 2-allyl-1-naphthol with dichlorobis(benzonitrile)palladium in 42 % and 22 % yields, III, b p 90°/8 mm, n m r (CCl₄) δ 2.40 (d, J=1 Hz, 3H), 6.55 (m, 1H), 7.2-7.9 (m, 6H), τ r 1601, 1580 cm⁻¹, m/e 182, IV, b p 70-72°/6 mm, n m r (CDCl₃) δ 2.48 (d, J=1 Hz, 3H), 6.41 (m, 1H), 7.1-8.3 (m, 6H), τ r 1602, 1580 cm⁻¹, m/e 182



III



IV

Since 2-propenylphenol could not be cyclized by the same reaction condition as above, obviously the cyclization proceeds not via first isomerization of starting olefin but the coupling of oxygen and β-carbon of allyl group

We thank Dr. P. Heimbach for valuable discussions

REFERENCES

- 1 D. S. Tarbell, Org. Reac., Vol. II, p. 18 (1944)
- 2 R. Adams and R. E. Rindusz, J. Amer. Chem. Soc., 41, 654 (1919), in this report the structure of 2-methylbenzofuran was incorrectly assigned as 2-methylenebenzofuran only by analysis. However, in Beilstein (Beil. Hand. Org. Chem., Vol. I, XVII, p. 25) it is correctly cited as 2-methylbenzofuran.
- 3 In this case, the yield was determined by integration of the n m r spectrum of the mixture obtained by distillation.